

# **DEFLUORIDATION OF DRINKING WATER USING ACTIVATED ALUMINA**

**A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY**

**By  
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**to the  
DEPARTMENT OF CIVIL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
AUGUST, 1978**

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# CERTIFICATE

This is to certify that the present study  
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Activated Alumina' has been carried out by Miss  
Madhu Rani Sharma, under our supervision and this  
has not been submitted elsewhere for a degree.

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## ACKNOWLEDGEMENT

It is with immense pleasure and great respect that I express my deep sense of gratitude to Dr. A.V.S. Prabhakara Rao and Dr. (Mrs.) Leela Iyengar, for their invaluable active guidance, inspiration and constant affectionate encouragement throughout this investigation.

I am highly indebted to Dr. C. Vencobachar for taking his time out of his busy schedule for valuable suggestions.

I am grateful to Dr. Malay Chaudhari, Ir. S.D. Bokil and Mr. D.N. Ghosh for their valuable suggestions and fruitful discussions from time to time.

It is beyond my words to express thanks to all my colleagues specially to S/s M.P. Pandey, I.R. Narbhar, R.D. Jain, P.C. Saini, S.M. Sadekar, Vinod Tare, T.I. Prakash for their help at all times in the course of present study.

The services rendered by Shri R.C. Adhikari is highly appreciated. Thanks are also due to N.R. Sahu, Ram Danch and S.N. Mishra.

I am highly thankful to Associated Cement Companies Ltd., Bombay, for supplying activated alumina.

DEFLUORIDATION OF DRINKING WATER  
USING ACTIVATED ALUMINA

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Several million people in smaller towns and villages of the country are using drinking water, the fluoride content of which lies in the toxic range ( $>1.5$  mg/l.). The observed impairment of teeth and bone deformation of these population justify the reduction of fluoride content of such water to the 'dental caries' preventing range of 1 mg/l.

Available literature indicated that studies conducted for the removal of fluoride in drinking water were inadequate to give a clear picture for their application in the field. The overall objective of this program was to evaluate the feasibility of activated alumina for the removal of fluoride and to collect some basic information for the design of a small household defluoridating unit. The results of the basic parameters and controlling factors studied, indicated the following useful information. Activated alumina is found to be excellent for the removal of fluoride. Fluoride removal efficiencies were

higher at pH lower than 6, reasonably constant in pH range 6-8 and decreased at pH values higher than 8. Alkalinity of the raw water was found to affect the removal efficiency adversely. Higher fluoride removal efficiencies were achieved at higher initial fluoride concentrations. An inverse relationship was observed between particle size and fluoride removal. Exhausted columns were regenerated by 0.1N HCl, 0.1N  $\text{H}_2\text{SO}_4$  and 1 per cent alum solution but  $\text{H}_2\text{SO}_4$  was the most efficient regenerant.

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## 1. INTRODUCTION

Water is one of the major environmental necessities for existence of life. Though there is an abundant supply of water on earth, only surface and ground water resources of fresh water are useful to man. Recent urbanization and industrial advancement have considerably deteriorated the surface water qualities resulting in increased utilization of ground water resources.

A very small percentage of Indian population living in urban areas is being served by protected water supplies. In most of the villages, water from wells having very poor quality are used for drinking purposes.

The physiological and toxic effects of chemical constituents of water depend on their concentration. Fluoride is now recognised, both in this country and abroad as a normal constituent of natural water and is 17th in the order of abundance of elements on earth's crust.

Fluoride in drinking water may be beneficial or detrimental depending on the concentration present. It is the most exclusive bone seeking element owing to its great affinity to calcium. Epidemiological studies have shown that there is an inverse relationship between fluoride concentration and 'dental caries'. Higher concentration results in the deposition of calcium fluoride in teeth and bones leading to dental and skeletal

fluorosis. It is now generally accepted that optimum fluoride concentration should be 1 mg/l. for the formation of strong teeth in children.

After the cause of dental fluorosis was identified, several methods were devised for removing excessive fluoride from water. Despite this situation only a few communities are known to be utilizing equipments specially installed to reduce the fluoride content. The situation may be attributed to a combination of several factors, most important being the high capital and running cost and the complexity of the removal processes.

The methods of fluoride removal which have been tried or suggested may be divided into two basic types - those based upon the addition of some material to the water during the softening or coagulation processes and those based upon ion-exchange or adsorption processes.

Additive methods include the use of lime, magnesia, calciumphosphate and aluminum sulfate (alone or in combination with a coagulant aid). Other materials such as bentonites, fuller's earth, diatomaceous earth, silica gel, bauxite, sodium silicate, sodium aluminate and ferric salts have also been tried. An appreciable removal with any of these materials was observed at low pH values ( $<3$ ) and at very high dosages.

The adsorption or ion-exchange processes involve the use of processed bone, activated carbon, magnesia, natural and synthetic ion-exchangers and activated alumina. All the materials

tried, however, possess one or more serious drawbacks, such as low capacities, difficult or expensive regeneration, high initial cost and lack of selectivity towards the fluoride ion.

The occurrence of water with high fluoride has been noticed throughout India. Majority of the dug well water in the villages (Devi Sawai Nagar, Nankari, Vinayakpur and Bairi village) around Lanpur have high content of fluoride and high incidence of dental fluorosis was observed in those areas.

A simple and cheaper defluoridation method is needed for the rural areas. The main objective of the present study is to develop a defluoridation method to overcome some of the above mentioned drawbacks. It is felt that it is very uneconomical to treat the entire water supply, because much of the water is used for washing and other domestic purposes where high fluoride is not objectionable. Therefore attempts are made to gather informations for the design of small house-hold defluoridating unit for drinking purposes.

## 2. LITERATURE REVIEW

Fluoride is regarded as an essential constituent in drinking water particularly for the prevention of dental caries in children. If fluoride concentration is less than 0.5 mg/l., a high incidence of dental caries is likely to occur. To prevent dental caries in children, a number of community water supplies are fluoridated abroad to bring optimum fluoride concentration.

Although an optimum amount of fluoride in drinking water is a valuable means for promoting dental health in children, excessive concentrations are associated with the hypoplasia of teeth, known as dental fluorosis. At much higher concentration, they may eventually cause endemic cumulative fluorosis with skeletal damage in both children and adults. The permissible concentration of fluoride in drinking water is 1.0 mg/l. (international standards, 1963).

### 2.1 Occurrence

The distribution of water containing high fluoride concentration is world wide. In several places in India, especially in Hyderabad (Daver, 1945), Madras (Kaghavachari et al., 1940), Andhra Pradesh (Murthy et al., 1953, Shroff et al., 1937), Punjab (Khan et al., 1945, Singh et al., 1962) and Rajasthan (Thergaonkar, 1974), fluoride content of drinking water exceeds the limit of safety.

Raghavachari and Venkataraman (1940b) have reported high fluoride content ranging from 2-7 mg/l. in water, in districts of Ananthapur, Cuddapan, Guntur, Kurnool and Nellore of Andhra Pradesh. Fluoride concentrations upto 1.5 mg/l. were also reported in some taluks of Nellore district where bone fluorosis was at its highest.

Pandit et al. (1940) have reported the incidence of mottled teeth in Ananthapur and Nellore districts of Andhra Pradesh and it varied from 50 to 90 per cent.

A high concentration of fluoride was observed by Rao and Bhaskaran (1964) in Kurnool district of Andhra Pradesh. The authors stressed on the need of a cheap defluoridating material suitable for rural areas based on initial pilot plant studies.

Thergaonkar and Bhargava (1974) studied the distribution of fluoride content in water in Jhunjhunu district of Rajasthan. They found that fluoride concentration in Rajasthan water varies from 0.1-18 mg/l. A high incidence of mottled teeth and fluorosis was also observed in those areas.

Excessive concentration of fluoride in well water has been reported by Chandrashekhra (1974) in different villages around Kanpur. In the four villages (Devi Sahai Nagar, Nankari, Virayakpur and Bairi) surveyed, routine chemical analysis of water drawn from 34 wells showed a fluoride content ranging from 0.7 - 3.5 mg/l. Ninety per cent of the water samples drawn from Nankari and Bairi village wells were found to

contain a fluoride content between 1.5-5.5 mg/l while only 25 per cent of water samples from other two villages, were found to contain fluoride content in excess of 1.5 mg/l.

A survey on fluorosis and dental caries showed that incidence of fluorosis was more than dental caries in these areas. Also, high incidence of fluorosis was reported in Nankari and Bairi villages than in Vinayakpur and Dahi Sahai nagar.

An attempt was made by Thergaonkar andulkarni (1971) to correlate the fluoride content and alkalinity. A positive correlation was observed between fluorides and alkalinity in ground water. Their studies indicated that water with fluoride concentrations above 1.5 mg/l. have high alkalinity also. The studies of Jolly et al. (1969) clearly indicate the dependence of incidence of skeletal fluorosis on pH, which in turn depends on alkalinity.

Venkatarayachari et al. (1971), have made an attempt to establish a relationship between fluoride concentration and the electrical conductivities of ground water. Although no linear relationship was noticed between the two variables it was inferred that water having more than 2 ppm of fluoride has electrical conductivities invariably more than 400 micro mhos cm. No such specific relationship was observed in water having less than 2 ppm of fluoride. This led to the conclusion that, in general, fluoride concentration of ground water in the endemic area show a direct relationship with the electrical conductivity.



## 2.2 Defluoridation Methods

Several methods were investigated for the removal of fluoride from drinking water by various workers from time to time. Defluoridation methods which have been tried or suggested may be divided into two categories:

1. Those based upon the precipitation of fluoride by adding materials to the water and also during the softening and coagulation processes.
2. Those based upon an ion-exchange or adsorption method.

### 2.2.1 Addition Methods

Additive methods involve the chemical precipitation of fluoride by the addition of some chemicals such as tricalcium phosphate, sodium silicate and also due to alum, lime and magnesium salt during the coagulation and hardness removal processes. Other chemicals such as bentonites, fuller's earth, diatomaceous earth, silica gel, bauxite, sodium aluminate and ferric salts have also been tried.

#### (a) Tricalcium Phosphate

Alder et al. (1938) found that it is possible to remove the fluoride by precipitating tricalcium phosphate in it. Tricalcium phosphate can be prepared from phosphoric acid and lime. Fluorides were reported to be almost completely removed, when lime and phosphoric acid were added so that the weight of the tricalcium phosphate precipitate was about two hundred times the

fluoride present. A controlled pH in the neighbourhood of 7.0-7.5 was required for the complete precipitation of tricalcium phosphate. The result of the studies showed the removal of 6.05 gr of fluoride per 1g tricalcium phosphate.

#### (b) Removal during coagulation process

Various authors have reported that coagulation process remove fluoride from water. Drop in fluoride content depends on the initial concentration of fluoride and on the type of the coagulant used.

Boruff (1934) conducted the coagulation experiments using alum and found that injurious amounts of soluble fluoride can be removed by dosing with alum, with subsequent removal of flocs by sedimentation and filtration. The data on the removal of fluoride using alum indicates that 4.0 ppm fluoride was removed from water when alum was used in concentration 170 ppm. Results showed that increasing dosages of aluminum sulphate gave proportionally greater removal of fluoride. Good mixing and good flocculation have been found to be necessary for the maximum removal of fluoride. Optimum pH was found to be 6.5-7.5.

McKee et al. (1934) made attempts to remove fluoride using iron and aluminum sulphate but they could not get appreciable removal. A reduction of the order of 0.25 ppm was observed when 165 ppm and 83 ppm of iron and aluminum sulphate were used, which was within the limit of error of the method.

According to Scott et al. (1937), it required 811 ppm of aluminum sulphate to reduce fluoride from 6 ppm to 1 ppm.

Culp et al. (1958) carried out the experiments with alum for the removal of fluoride. Basically his method consisted of application of 295 ppm of alum in increment during rapid mixing. The formed flocs were allowed to settle and were passed through rapid sand filters. A reduction from 4 to 1.5 ppm was observed in effluent.

Results reported on the effectiveness of aluminum hydroxide flocs formed from aluminum sulphate and a source of alkalinity vary considerably. The variation can be attributed to such factors as the following: different rawwater with varying initial concentrations were used, the speed of adding the reagents and method of mixing were different, time of contact was varied, pH was not the same and not all the effluents were filtered.

Treatment of natural waters containing fluoride with alum however, gave much less removal. An investigation was undertaken by Boruff et al. (1937) to study this discrepancy in results. Results indicated-

(1) Cation associated with the fluoride ion in water greatly affect the completeness of its removal by alum flocs and hence this method is not applicable to defluoridation of many natural waters.

(2) The removal of calcium and magnesium ion by zeolite treatment is not sufficiently complete to convert small amounts of fluoride to sodium fluoride. Therefore, softening of water with zeolite before alum treatment does not materially improve fluoride removal.

Nawlakhe et al. (1974) studied the usefulness of alum in removing fluoride from drinking water and brought out the scope of its application in field.

The same group of authors in 1975 developed a technique, referred as 'Nalganda Technique', which comprises addition in sequence of sodium aluminate or lime and filter alum to fluoride water followed by flocculation, sedimentation and filtration. Bleaching powder was added to ensure disinfection and lime hastens settlement of precipitate. The data indicated that ratio of fluoride removal from water to the quantity of alum applied varies from 0.0725 - 0.1380 with an average value of 0.1127. The lime dose required in this process was 1/20th - 1/25th that of filter alum. The presence of  $\text{SO}_4^{=}$ ,  $\text{Ca}^{++}$ ,  $\text{Cl}^{-}$  etc. were not found to affect the process adversely.

Further, attempt was made by Nawlakhe et al. (1978) to find out the effect of various parameters such as polyphosphates, nitrates, silicates, organic matter and temperature on the removal of fluoride by Nalgonda technique. Polyphosphates, nitrates and organic matters have no adverse effect on this technique but silicates and temperature, decrease the efficiency of removal.

Fluoride removal experiments in which aluminum sulphate and coagulant aids (clays, activated silica) used together were conducted in the Industrial Hygiene Laboratories at the National Institute of Health and in pilot plants at Great falls, Md (Meier, unpublished work). The results of the conventional type of plants at Great falls indicated that fluoride concentration can be decreased in two steps (6-3.5 ppm and from 3.5 - 1 ppm) using in each step 100 ppm aluminum sulphate, 100 ppm clay and about 25 ppm of lime.

When activated silica (Baylis sol) was used in conjunction with alum, clay and soda, a further, reduction in fluoride was noticed (Hay, 1944). The process was not efficient with highly mineralised ground water containing excessive fluoride content.

Removal of fluoride during ferric chloride coagulation was also studied. Results indicate that 34-85 ppm of  $\text{FeCl}_3$  for water containing 1.8-5.0 ppm of fluoride at a pH 7.2 gave small removal (Boruff, 1934). Ferric fluoride complex is only slightly ionized and therefore there is a chance that fluoride may be removed by this coagulant.

Sodium aluminate, when used as coagulant, gave very small amounts of fluorides. A dose of 24,44 ppm was found to reduce the fluoride content of 5 ppm to 4.8 ppm and 4.4 ppm respectively (Boruff, 1934).

Other methods utilizing aluminum salt involve contact beds of insoluble materials impregnated with alum. Bhakuni et al. (1962) have reported that the activated carbonized saw dust can be used for fluoride removal after quenching it in 2 per cent aluminum sulphate for 15 minutes. When 2 gm of material was added to 50 ml of 5 ppm fluoride solution, a reduction of 4.2 ppm of fluoride was observed. With alum, however, 3.5 ppm was removed under the same experimental conditions.

Seethapathi Rao (1964) employed sulphonated coconut shell carbon for alum impregnation. The data reported in the article indicate that 20 g of the carbon could treat about 1.5 litres of water (initial fluoride concentration, 2.5 mg/l.).

### (c) Removal during softening process

The use of lime for fluoride removal was first of all investigated by Boruff (1934). Coprecipitation of fluoride was brought about by treating water with lime to cause precipitation of magnesium hardness. Result of the test conducted indicated that 5 ppm of fluoride was reduced to 3 ppm.

In a study of lime softening plants in Ohio (Scott et al., 1937), it was determined that fluoride reduction with lime is a function of amount of magnesium removed. It was demonstrated that as the pH is raised during softening, the magnesium in water is precipitated as hydroxide which adsorbs the fluoride from water.

A definite relationship between fluoride reduction and magnesium removal which holds good for initial fluoride concentrations of 1.5 - 3.5 mg/g was established. The relation is

$$\text{Fluoride reduction} = 7 \text{ per cent of the initial concentration} \times \sqrt{\text{Mg removed}}$$

In terms of residual fluoride, the relation is

$$Y = F - (0.07\sqrt{C})$$

where Y = residual fluoride, mg/l.

F = initial fluoride, mg/l.

C = magnesium removed, mg/l.

Theoretically, if a residual fluoride of 1 ppm is desired, 100 ppm of magnesium must be removed if initial concentration of fluoride is 3.3 ppm. A magnesium concentration of this magnitude is rare in most of the waters containing high fluoride content. Therefore employment of this method involves the addition of magnesium preferably in the form of dolomite lime and activated magnesia.

The addition of 2 g of magnesium chloride to 1 litre of water containing 15 ppm of fluoride was reported to reduce fluoride to 3 ppm (Paluch and Kozodzig, 1965).

Instead of soluble magnesium salt, particulate salts of magnesium having low solubility was employed by Augusto (1967). Experimental set up having two containers connected in series was used. The water and partially formed sludge, which was

formed in the first container when test water and magnesium salt was introduced, was directed to second container to allow the settlement of sludge. The supernatant from second container was introduced to first container with fresh magnesium salt. The process was repeated until the fluoride content in the water was reduced considerably.

Thergaonkar et al (1971) carried out experiments for fluoride removal using magnesia and found that upto a fluoride concentration of 7 mg/ l., there was no reduction in fluoride content with 0-500 mg/l. magnesia. At higher concentration of fluoride (10 - 15 mg/l. ) about 50 per cent reduction was obtained with 500 mg/l. magnesia. Even 1500 mg/l. magnesia was not found to reduce the fluoride to 1.2 mg/l.

## 2.2.2 Ion Exchange and Adsorption Methods

The materials used in contact beds, include synthetic or natural ion-exchange materials, processed bone, tricalcium phosphate, activated carbon and activated alumina.

### (a) Ion exchange materials

Compounds, which are subjected to aluminum sulphate solution soaking, probably involve a combination of ion-exchange and adsorption. An additional group of defluoridation products depend on ion-exchange property entirely. A large number of these materials have been developed, many of them patented and their relative merits have been calculated.



The use of a strongly basic anion exchange resin in the chloride form promises a new approach to this problem, as indicated by the studies of Thomson (1953). The effectiveness of the treatment depends on the concentration of fluoride. Removal capacity of approximately 40 g/cu.ft. of resin was obtained when raw water has a fluoride - total anion ratio of 0.0147. The resin was regenerated by sodium chloride.

Shannikov (1961) reported that anion exchange resins remove fluoride from water down to permissible level. Previous passage of water through the  $H^+$  form of a cation exchange resin increases fluoride removal.

The behaviour of fluoride during ion-exchange treatment was studied by Neoskaya (1961) with a fluoride content of 3.8-7.0 mg/l. Water was passed successively through the cation exchanger and anion exchanger. The fluoride in an average sample of water was 1.5 mg/l.

Sastri (1963) prepared cation exchangers from waste materials like paddy husk, tea waste, jute waste and ground nut shell by sulphonation under suitable conditions. These materials after treatment with sodium carbonate and alum were found to remove fluoride from water. Results show that tea waste carbon possess the highest removal capacity.

Popa et al. (1968) conducted the fluoride removing experiments using strongly basic ion-exchangers such as Merk II and got the desired fluoride in the effluent.

## (b) Activated carbon

The importance of application of activated carbon in water treatment processes as taste, colour and odour removal has been recognised long back.

McKee et al. (1934) were the first to use carbon for the removal of fluoride from drinking water. The chief drawback of their work was that even with the most active carbon, there was no removal of fluoride until the pH of the water had been reduced to 3. At this pH 90 per cent fluoride was reported to be removed. Attempts to reduce fluoride content of water with high pH, upto 1 ppm have been unsuccessful.

Phakuni et al. (1963) prepared carbon from abundantly available raw material, saw dust, using the process of carbonisation. The defluoridating capacity was found to be 350-450 mg/l of dry material (initial concentration 4.5-5 ppm). Other ions as  $\text{Cl}^-$  and  $\text{SO}_4^{=}$  appear to influence the removal of fluoride from water by this method. The fluoride removal capacity was lower when natural water containing high amount of dissolved solids was used.

Experiments on the use of activated carbon was conducted by Seth (1965). Results indicated that activated carbon of mesh size between 20-40 (BSS) and a time factor of 10-15 minutes gave the maximum removal. Suggestions were also made for the design of a simple home defluoridating unit which will be suitable for a family of 4 to 5 people having the water requirement of 2-3 gallons per day.

### (c) Tricalcium phosphate

The use of bone was one of the earliest method suggested for the removal of fluoride. The use of bone for removing fluoride is based on the long known affinity of bone for calcium. Perhaps the most logical explanation for this reaction involves the anion exchange properties of apatites. The carbonate radical of the apatite comprising bone,  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaCO}_3$ , is replaced by the fluoride forming insoluble fluorapatite. During the regeneration of the material with sodium hydroxide, fluorapatite probably becomes hydroxyapatite and the sodium is removed in the form of soluble fluoride. The hydroxy apatite subsequently becomes available as exchanging material by the replacement of  $\text{OH}^-$  group with fluoride. Tricalcium phosphate, principle constituent of bone, was used in the form of bed by various workers.

Alder (1938) made the use of precipitated and dried tricalcium phosphate bed. The highest capacity found was 3.5 g/kg of tricalcium phosphate. It was reported that washing the exhausted adsorbent with sodium hydroxide, followed by hydrochloric acid rinse, restored the adsorptive property. A 50 percent reduction was observed after 10 cycles of regeneration. The removal capacity was found to decrease sharply as hardness of water was increased.

Using this method of regeneration and neutralisation, a loss of 3-4 per cent of the tricalcium phosphate was reported per regeneration. Behram et al. (1938) suggested a modified

method of regeneration, comprising the use of carbon dioxide in place of hydrochloric acid for neutralising the excess alkali. The fluoride removal capacity of the tricalcium phosphate was unchanged for a long period and after a large number of regeneration cycles no appreciable change in the weight was reported.

Goodwin and James (1941) did a pilot plant study with carbon dioxide as the neutralising agent for excess alkali. The capacity of the tricalcium phosphate was found to be 275 grain/cu.ft. After 50 cycles of regeneration, 1.5 per cent loss in wt. was observed. Therefore, he suggested that 5 per cent phosphate replacement might be necessary after 100 cycles of regeneration.

Tricalcium phosphate, bone char and bone meal beds were employed at different treatment plants in Southern California (Harmon et al., 1965). Among these, tricalcium phosphate was found to be the best. Caustic soda was used for regeneration. For neutralisation, a number of different chemicals were tried including phosphoric acid, sulphuric acid, carbon dioxide, hydrochloric acid and sodium sulphate. Caustic soda and carbon dioxide regeneration were found to be the best.

#### (d) Activated alumina

The use of a bed of aluminum oxide for the removal of fluoride ion from drinking water was first suggested by Boruff (1934). After the exhaustion of activated alumina bed, it was regenerated by 2 per cent solution of sodium hydroxide, followed

by neutralisation of the excess alkali with dil. HCl. Calculation based on the data present indicates that the capacity of the alumina was about 295 grain/cu.ft. of alumina. Regeneration with 5 per cent sodium chloride and 2N HCl gave results which were approximately same as noted in the sodium hydroxide regeneration. 2N HCl caused loss in the weight of activated alumina. Sodium chloride was proposed to be a suitable regenerant to use.

The activated alumina has been tried in the field tests and rated as fairly good with respect to fluoride removal efficiency. Fink and Lindsay (1936) conducted the studies to demonstrate the effectiveness of a specially prepared alumina for the removal of fluorides. Efforts were also made to adopt this process to a unit which could be used in the house for treating the required quantities of water. The capacity of the material was calculated to be about 416 grainfluoride/cu.ft. of alumina. Sodium chloride exhibited practically no regeneration effects and solutions acidified with HCl and HCl solutions (1 per cent ) was reported to restore only 90 per cent of the original efficiency. Complete regeneration was accomplished with 8 per cent solution of sodium hydroxide or with an alkaline solution of sodium aluminate containing a total alkalinity equivalent to 8 per cent of sodium hydroxide.

Swope and Hess (1937) reported on the use of activated alumina for the removal of fluoride. Regeneration of this material was done with a 5 per cent sodium hydroxide solution followed by neutralisation with 0.35 per cent hydrochloric acid.

From the data presented, exchange capacity of this product was calculated to be 505 grain fluoride/cu.ft. of material.

Finding of these authors, enhanced the progress of defluoridation of water. In March 1952, a new plant was put in operation at Barlett, Texas, in which fluoride content of the raw water was reduced from 8 - 1 ppm (Lee, 1952). Bed was regenerated for two hours by (1) Back washing to remove foreign matter retained on the alumina; (2) forcing caustic soda solution through the alumina; (3) followed by washing with water and then with a weak sulphuric acid solution. Similar studies were also conducted by Maier (1947) and Harmon et al. (1965)

Savinelli et al (1958) conducted an exhaustive screening programme of various regenerants and found that dilute solution of aluminum sulphate alone could be used to regenerate alumina. It was also reported that when alumina was regenerated in this manner, it had an appreciably higher fluoride exchange capacity than when treated by any other previously maintained methods. The exchange capacity of the alumina was found to be proportional to the amount of the filter alum used for regeneration upto a level of 12 lb. alum/ cu.ft. of alumina. Fluoride removing capacity was found to be 20 per cent of the original at alkalinity values 200 mg/l. (as  $\text{CaCO}_3$ ). Exchange capacity was found to be independent of both regenerant concentration and flow rate. The mechanism of regeneration was reported as ion exchange process.

Thergaonkar et al. (1969) developed a medium named 'Defluoron 2' for the reduction of fluoride in water supplies which works on aluminum cycle. Alum was used for regenerations and higher fluoride removal efficiency (380 mg/kg) was achieved with 5 per cent alum. Alkalinity of the raw water was found to have an adverse effect on fluoride removal capacity. Fluoride removal efficiency was observed to be 20 per cent of the original at alkalinity value 500 mg/l. (as  $\text{CaCO}_3$ ). The clogging problems were observed at some places during column study.

Bishop et al. (1975) made an attempt to overcome this problem of clogging of bed by using a fluidized activated alumina bed for fluoride removal. Fluidized activated alumina exhibited excellent characteristics for the removal of fluoride from water. A capacity greater than 1000 grains of fluoride per cubic ft. of media (2.3 kg/cu.m.) both achieved with 30-50 mesh media size. A low pH and high fluoride content enhanced fluoride removal. The only parameter which was found to effect removal efficiency adversely was alkalinity and 80 per cent reduction in the efficiency was observed at alkalinity value 500 mg/l. (as  $\text{CaCO}_3$ ). Results indicate that for a water containing 10 mg/l. fluoride, an alkalinity of 35 mg/l. (as  $\text{CaCO}_3$ ) and a loading rate of 12 gpm/sq.ft. and activated alumina media depth of 8-10 inches (20-25 cm) provides maximum removal of fluoride.

Kazuo (1976) conducted experiments for the selective removal of fluoride from water containing various types of

ions. Fluoride containing water was treated with hydrochloric acid treated alumina,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{ZnO}$ . Comparatively better fluoride removal was obtained with treated alumina than with untreated.

### 2.3 Adsorption on Activated Alumina

Alumina ore or bauxite, characteristically occurs in nature as an impure weathering product of aluminous rocks. Alumina can exist in a number of hydrated and dehydrated crystalline modification. Activated aluminas are generally  $\gamma$ -alumina.

Commercial alumina is prepared by temperature (approx.  $700^\circ\text{C}$ ) dehydration of alumina trihydrate and is a mixture of  $\gamma$ -alumina and some alumina monohydrate ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) (Vander Werf et al. 1963). However, aluminas heated above  $1000^\circ\text{C}$  are converted to inactive  $\alpha$ -alumina.

#### 2.3.1 Structure of $\gamma$ -Alumina .

Aluminum ion is trivalent ( $\text{Al}^{3+}$ ) and is in six-fold coordination with oxygen so each oxygen receives only a half valency share from  $\text{Al}^{3+}$ . Each oxygen, therefore, receives half valency share from each of the four  $\text{Al}^{3+}$  (Grimsaw, 1971).

#### 2.3.2 Origin of Surface Charge.

While it is not possible to specify the exact nature of adsorption sites on activated alumina, it has been suggested



that these are exposed aluminum atom, strained Al-O bonds or other cationic sites on the surface of activated alumina (Heftmann, 1975). There seems to be two types of anion exchange mechanism.

1) Replacement of  $\text{OH}^-$ , Buswell et al. (1941) presented strong evidence, based on infrared absorption and have shown that the  $\text{OH}^-$  of alumina surface can enter into exchange reactions

2) The recent hypothesis for the anion exchange depends on the presence of anion exchange spots on the surface of alumina (Hunter et al., 1963). Such anion exchange positions would be due to unbalanced charges within the lattice, e.g., an excess of aluminum ion in the octahedral (Grim, 1963).

Kubli (1947) found the anion alumina adsorption series, in order of decreasing preference, to be  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{MnO}_4^-$  and  $\text{SO}_4^{2-}$ .

### 3. SCOPE OF INVESTIGATION

A review of the literature given, shows the presence of excessive concentration of fluoride in drinking water resulting in the high incidence of fluorosis. Majority of the dug well water in the villages around Kanpur have fluoride content more than 1.5 mg/l.

The removal of excessive amount of fluoride from a community drinking water is a necessary procedure for the prevention of endemic dental fluorosis. Several methods have been devised from time to time for the removal of fluoride from drinking water but all are found to have one or other drawbacks.

A simple device that can be used for rural population seems to be the need of the day. One such device could be a cartridge or column containing efficient defluoridating material capable of being regenerated by individual users or by a central place in the block development office. Hence the present study includes screening of available materials for defluoridation and evaluation of activated alumina produced in the country for basic and important characteristics needed for the development of a cartridge or column. It is hoped that advantage will be taken of this to ameliorate the condition of thousands of people who are today exposed to fluorosis in India.

## 4. MATERIALS, METHODS AND EXPERIMENTS

### 4.1 Materials

Hornblende and Stilbite were supplied by 'Alminrock Indsco Fabriks', Malleswaram, Bangalore. Alumina (chromatographic grade) and partially activated carbon was purchased from Sarabhai M. Chemicals Pvt. Ltd., Wadi Road, Baroda and Lakshmi Carbons, Najibabad, U.P., respectively. Bentonite, Montmorillonite and Bauxite were provided by Soil Mechanics Laboratory, Indian Institute of Technology, Kanpur. G-80 grade activated alumina was supplied by Associated Cement Companies Limited, Bombay in the form of globules of 5-7 mm diameter. The general properties of activated alumina is given in Table 1.

The raw water used for the experiments was drawn from two sources. (i) distilled water and (ii) tap water, campus water supply, Indian Institute of Technology, Kanpur. The water supply to the campus is maintained from five deep tube wells situated within the Institute premises. The average characteristics of tap water are tabulated in Table 2.

All other chemicals used during this experimental work were of analytical grade.

### 4.2 Methods of Analyses

(a) Estimation of Fluoride. Fluoride was estimated using alizarin photometric method according to standard methods for the examination of water and waste water (12th edition).

Table 1. General properties of activated alumina<sup>#</sup>


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Surface area (MIN)m <sup>2</sup> /gm	230
Pore volume cc/gm	0.29-0.35
Bulk density (loose) kg/ l.	0.90
Bulk density (packed) kg/l.	1.05
Crush strength (average point load in Kgs on 5 mm diameter)	8-12
Loss on attrition	0.3
Water adsorption capacity (wt. per cent):	
A. at 15 per cent RH and 30°C	5-5.5
B. at 60 per cent RH and 30°C	14-16
Chemical Analyses:	
Al <sub>2</sub> O <sub>3</sub>	93
Na <sub>2</sub> O	0.7
Fe <sub>2</sub> O <sub>3</sub>	0.1
SiO <sub>2</sub>	0.1
Loss of Ignition (at 1100°C)	6.0

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<sup>#</sup> Information supplied by Associated Cement Companies Limited,  
Bombay.

Table 2: Average characteristics of I.I.T. Kanpur tap water

Characteristics	Concentrations
pH	8.4
Total Alkalinity (as $\text{CaCO}_3$ )	500 mg/l
Total Hardness (as $\text{CaCO}_3$ )	168 mg/l
Calcium (as $\text{CaCO}_3$ )	135 mg/l
Magnesium (as $\text{CaCO}_3$ )	33 mg/l
Carbonates (as $\text{CaCO}_3$ )	0 mg/l
Bicarbonates (as $\text{CaCO}_3$ )	500 mg/l
Fluoride	1 mg/l
Sulphate (as $\text{SO}_4^{=}$ )	60 mg/l
Chloride (as $\text{Cl}^-$ )	100 mg/l

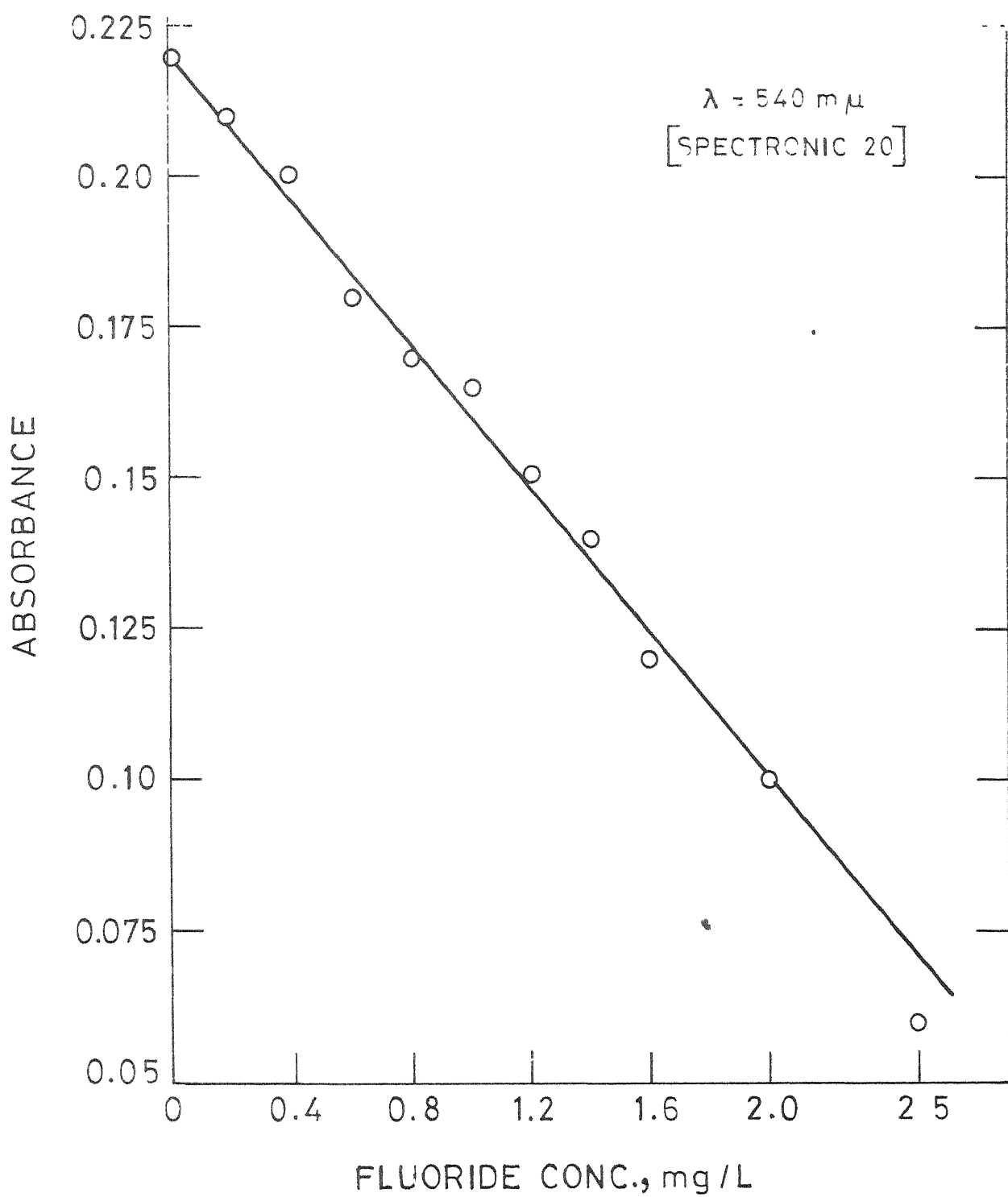


FIG 41. STANDARD CURVE FOR FLUORIDE TEST

calibration curve was prepared by diluting appropriate quantities of standard fluoride solution (0.2210 gr anhydrous sodium fluoride dissolved in one litre of distilled water) to 100 ml with distilled water in the range 0.00 to 2.50 mg/l. 5 ml of alizarin red solution (0.75 gm 3-alizarin sulphonic acid sodium salt dissolved in one litre of distilled water) and 5 ml of zirconyl acid reagent (0.30 gm of zirconyl oxychloride octahydrate dissolved in 1 litre of distilled water containing 33.3 ml of sulphuric acid and 101 ml of hydrochloric acid) were added. Absorbance was measured after 60 minutes at 540 mμ using Spectronic 20. Calibration curve is shown in Fig. 4.1.

(b) Measurement of pH : pH of the sample was measured by expanded scale pH meter, type 331 model, SYSTRONICS.

(c) Estimation of other ions: All other ions such as  $\text{CO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{=}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  were estimated according to standard methods.

### 4.3 Experiments.

#### 4.3.1 Preliminary Studies

To select the most efficient adsorbent for fluoride removal, 1 gm of each adsorbent was suspended in known amount of fluoride solution. Particle size of all adsorbents were 0.21-0.42 mm except alumina (0.10 - 0.12 mm particle size). 0.1N HCl was used for the pretreatment of alumina. The selected

adsorbents were used for all further experiments.

Experiments were carried out for the determination of optimum amount of alumina for the removal of fluoride in batch studies. Different reactors were set up containing the same volume of fluoride solution with different amounts of alumina ranging from 0.1 gm to 2.0 gm. Fluoride was determined in the supernatant after suitable contact time.

Studies were conducted for the removal of fluoride using both agitated non-flow system and continuous-flow system.

#### 4.3.2 Agitated Non-flow Studies

Agitated non-flow studies were carried out to study the kinetics of adsorption, effect of pH, particle size, initial fluoride concentrations and alkalinity on the removal of fluoride. Fluoride solutions were prepared by adding the known amount of sodium fluoride to distilled water (except in the case of alkalinity effect where tap water was used for the preparation of samples). For all agitated non-flow studies 100 ml of 8 mg/l. fluoride solution was taken in a stoppered glass bottle of 300 ml capacity. Activated alumina of particle size 0.21-0.42 mm was employed. Rotatory shaker was used to ensure thorough mixing.

4.3.2.1 Adsorption kinetics: This experiment was carried out with activated alumina. 0.2 gm of the material was suspended in known volume of fluoride solution. An aliquot was taken at



regular intervals upto 60 minutes and fluoride was determined in the supernatant. The optimum contact time was used for all further experiments.

4.3.2.2 Effect of pH: A pH range of 2 - 9 was selected to study the effect of pH on fluoride removal. pH was adjusted by adding sulphuric acid or sodium hydroxide to the sample. 0.2 gm of activated alumina, which was found to be optimum, was added to each bottle and after 15 minutes of contact time, fluoride was determined in the supernatant.

4.3.2.3 Effect of alkalinity: Tap water alkalinity was found to be around 500 mg/l (as  $\text{CaCO}_3$ ). Tap water was diluted with distilled water to prepare the sample water with alkalinity ranging from 100-500 mg/l (as  $\text{CaCO}_3$ ). A control with distilled water was also used. After 15 minutes of contact time with 0.2 gr of activated alumina, fluoride was determined.

4.3.2.4 Effect of particle size: In order to determine the most efficient media particle size for fluoride removal, activated alumina was ground and sieved and particles of sizes 0.42-0.85, 0.21-0.42 mm, 0.12-0.21 mm, and 0.10-0.12 mm were collected. 0.2 gm of the material was added to different bottles, each containing a known volume of fluoride solution. Removal of fluoride was determined after 15 minutes.

4.3.2.5 Effect of initial fluoride concentration: To study the effect of initial fluoride concentration, samples containing different fluoride concentration ranging from 1-15 mg/l, were added to different bottles containing 0.2 gm of activated alumina and fluoride was determined in the supernatant after 15 minutes.

#### 4.3.3 Continuous Column Studies :

Down-flow column studies were carried out for fluoride removal using the activated alumina of particle size 0.21-0.42mm. Fluoride solutions prepared in distilled water were used to study the effect of flow rate and regeneration on fluoride removal capacity of activated alumina. For rest of the studies, fluoride solutions prepared in tap water were used. Constant flow was maintained and checked throughout the run. Two sizes of the column were employed for different experiments.

i) Small size column: The column used consisted of glass tube of approximately 10 mm diameter and 60 cm length. The quantity of activated alumina used was around 10 gr which formed a bed of approximately 16 cm depth.

ii) Large size column The column consisted of perspex tube of approximately 2.7 cm diameter and 35 cm long. 100 gm of the alumina was filled in the column. The height of the activated alumina was 24 cm.

4.3.3.1 Regeneration: 0.1N HCl, 0.1N  $H_2SO_4$  and 1 per cent alum were tried as regenerants. Columns were regenerated when a leakage of more than 1.5 mg/l. of fluoride was observed in the effluent during the course of column run. Regenerant was passed through the column at a constant rate of 100 ml/hr. After the regeneration, columns were thoroughly washed with distilled water before using for fluoride removal.

The suitable amount of regenerant was determined by passing one litre of 0.1N HCl through the column and estimating the fluoride content in the effluent. This could not be repeated with sulphuric acid and alum as  $SO_4^{=}$  was found to interfere with the fluoride determination method.

4.3.3.2 Selection of suitable regenerant: Small size columns were used. Three columns packed with activated alumina were used for fluoride adsorption. A constant flow (37 lpm/sq.m) was maintained throughout the column run. Column runs were terminated when the fluoride leakage exceeded the limit of approximately 1.5 mg/l. Columns were regenerated with HCl,  $H_2SO_4$  and alum solution and were washed with distilled water thoroughly. Fluoride removal capacity of activated alumina was determined in each case.

The above experiment was repeated using fluoride solution prepared in tap water. Columns were operated at higher flow rate (140 lpm/sq.m.). 15 Cycles of regeneration were carried out for HCl and  $H_2SO_4$ , to study the effect of regeneration cycles on the fluoride removal capacity of activated alumina.

4.3.3.3 Effect of flow rate: Different columns were used and operated at different flow rates (37 lpm/sq.m., 70 lpm/sq.m., and 140 lpm/sq.m.). Fluoride removal capacity of the column was determined in each case.

4.3.3.4 Optimum concentration of regenerant: Different concentrations of sulphuric acid, ranging from 0.05-0.5 N were used to regenerate the columns. Separate columns were employed for each concentration and fluoride removal efficiency of activated alumina was determined after regeneration with each concentration of acid.

Smaller columns were regenerated using different bed volumes of  $H_2SO_4$  for different contact times and fluoride removal efficiency was determined. 5 Cycles of regeneration were conducted using one bed volume of the acid.

After the preliminary program of experiments with small size column, large size column was tried. The column was operated at a constant flow rate of 140 lpm/sq.m. Column was regenerated by one bed volume of sulphuric acid for 30 minutes and 60 minutes contact time and fluoride removal efficiency was determined.

## 5. RESULTS AND DISCUSSION

All experimental results are presented in either graphical or tabular form. In order to facilitate the presentation, a discussion of the result follows each phase of experimental work.

First step of the study was to select some material for the removal of fluoride and then to study the effect of various parameters for the removal of fluoride using that material.

### 5.1 Selection of Adsorbent:

Various adsorbents were tried for the removal of fluoride from water. Results are shown in Fig. 5.1. Excepting two materials of the total nine used, all gave removal efficiency less than 50 per cent. Alumina by itself gave only 38 per cent but the efficiency increased to hundred per cent after acid(HCl) treatment. Interestingly activated alumina without any pre-treatment gave the same efficiency. Hence the following experiments were conducted by these materials only.

Further, experiment was carried out with varying amount of material to find optimum amount. As expected results show an increase in the fluoride removal as the amount of activated alumina and acid treated alumina was increased. An amount of 0.2 gm is found to be optimum for both and employed for further experiments (Fig. 5.2).

Among activated alumina and acid treated alumina, the former is selected for the rest of the experiments for the

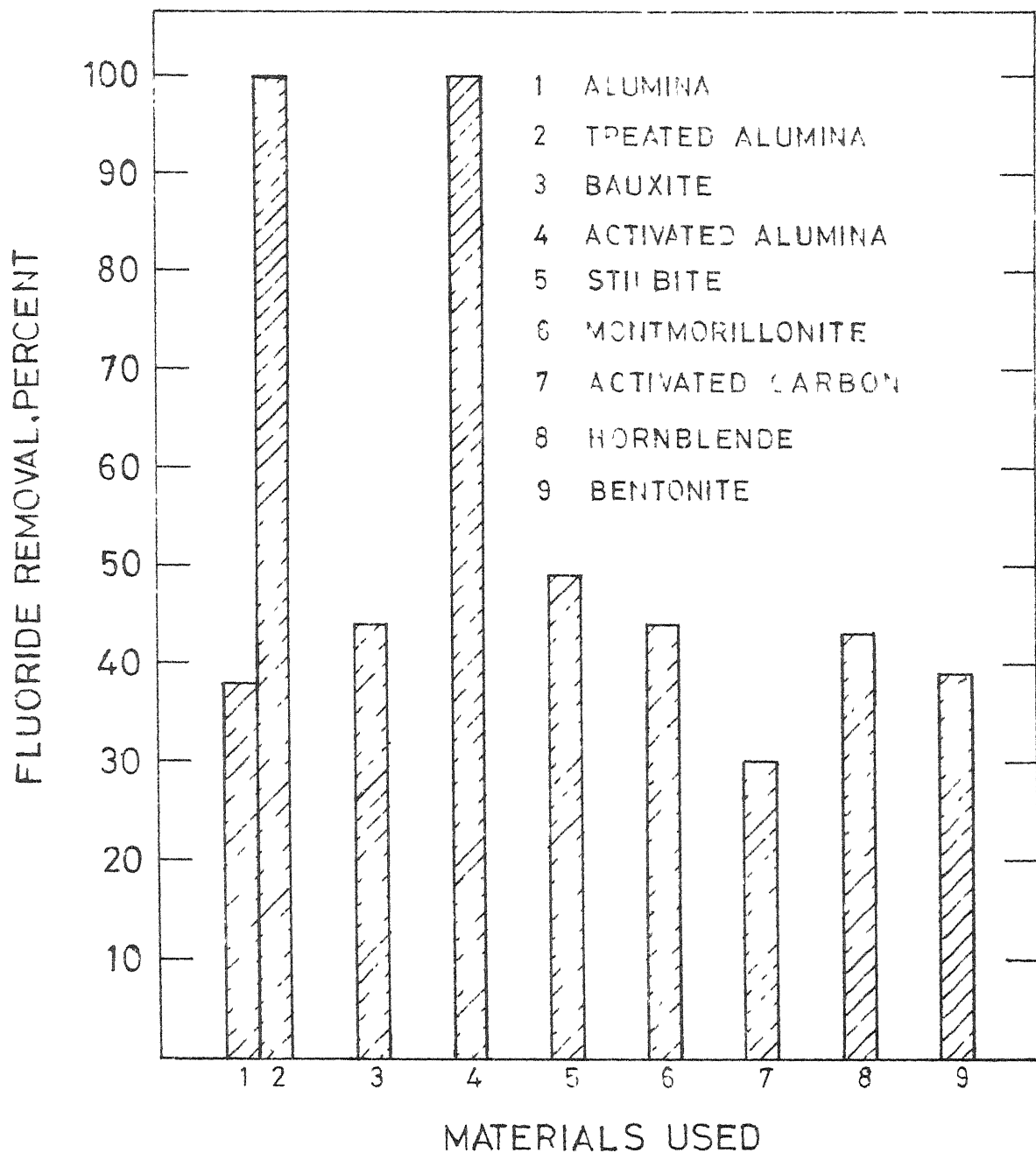


FIG.5.1 REMOVAL OF FLUORIDE BY DIFFERENT MATERIALS

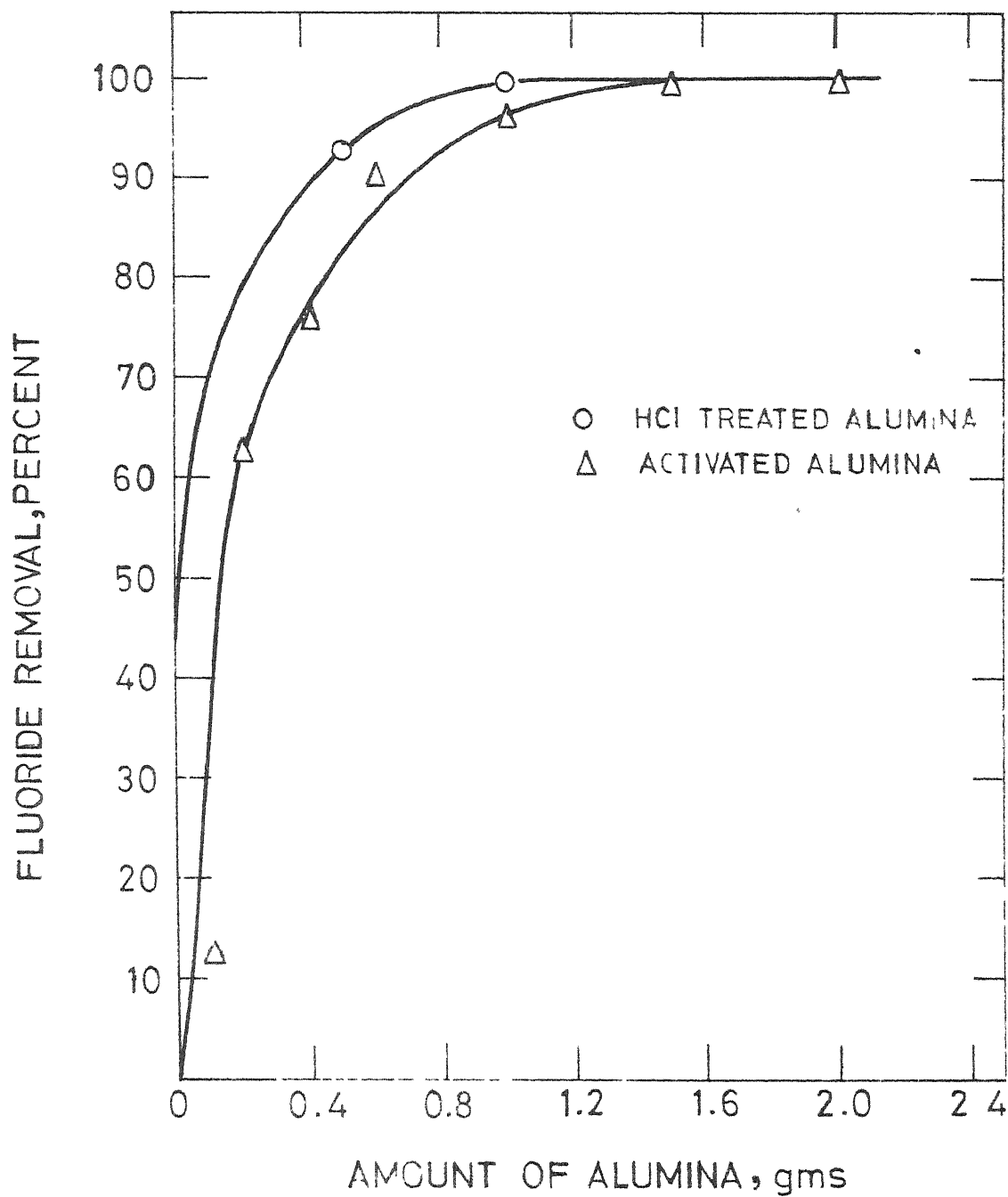


FIG.5.2 DETERMINATION OF OPTIMUM AMOUNT OF ALUMINA FOR FLUORIDE REMOVAL

following reasons:

i) Activated alumina was found to remove fluoride efficiently without any pretreatment.

ii) Alumina was available in the particle size range 0.21-0.12 mm which is too small for column studies.

iii) Alumina used was more expensive as compared to activated alumina.

Experiments on the removal of fluoride by activated alumina were conducted using agitated non-flow studies and continuous column studies.

## 5.2 Agitated Non-flow Studies.

### 5.2.1 Adsorption Kinetics

Adsorption kinetic studies were carried out to find the optimum contact time for fluoride removal and also to know the exact mechanism of adsorption i.e., whether it is film diffusion or intraparticle diffusion. Theoretical treatment on the kind of diffusion yields rather complex mathematical relationship. However, a quick method to know the mechanism is to plot a graph between the sorbent uptake and the half power of time (Weber, 1971). Plot (Fig. 5.4) does not represent a linear relationship. It suggests that removal of fluoride takes place only at the surface and does not involve any slow penetration into fine internal pores. 15 minutes is selected as the optimum contact time for fluoride removal for all further studies (Fig. 5.3).



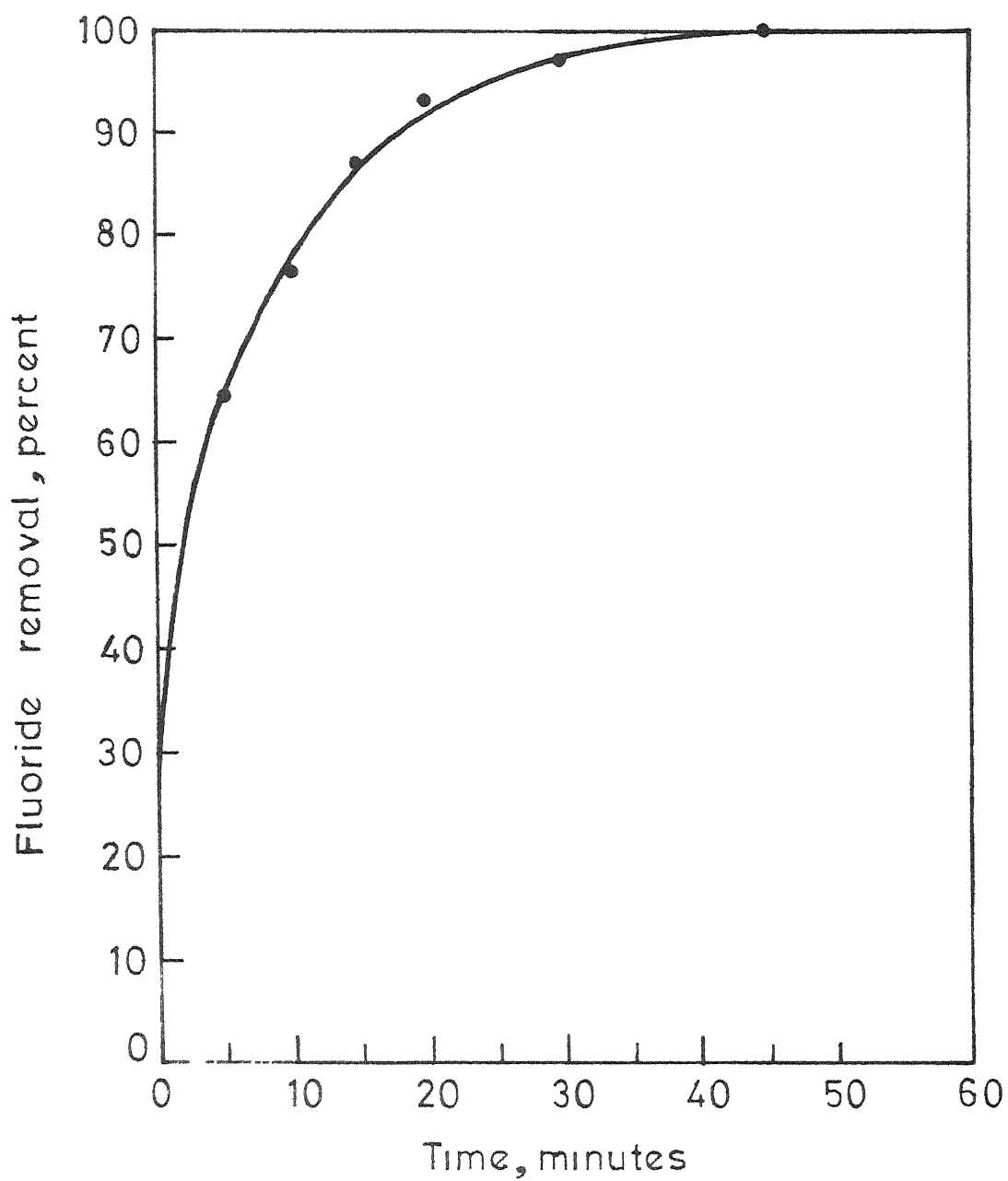


FIG.53 KINETIC STUDY WITH ACTIVATED ALUMINA.

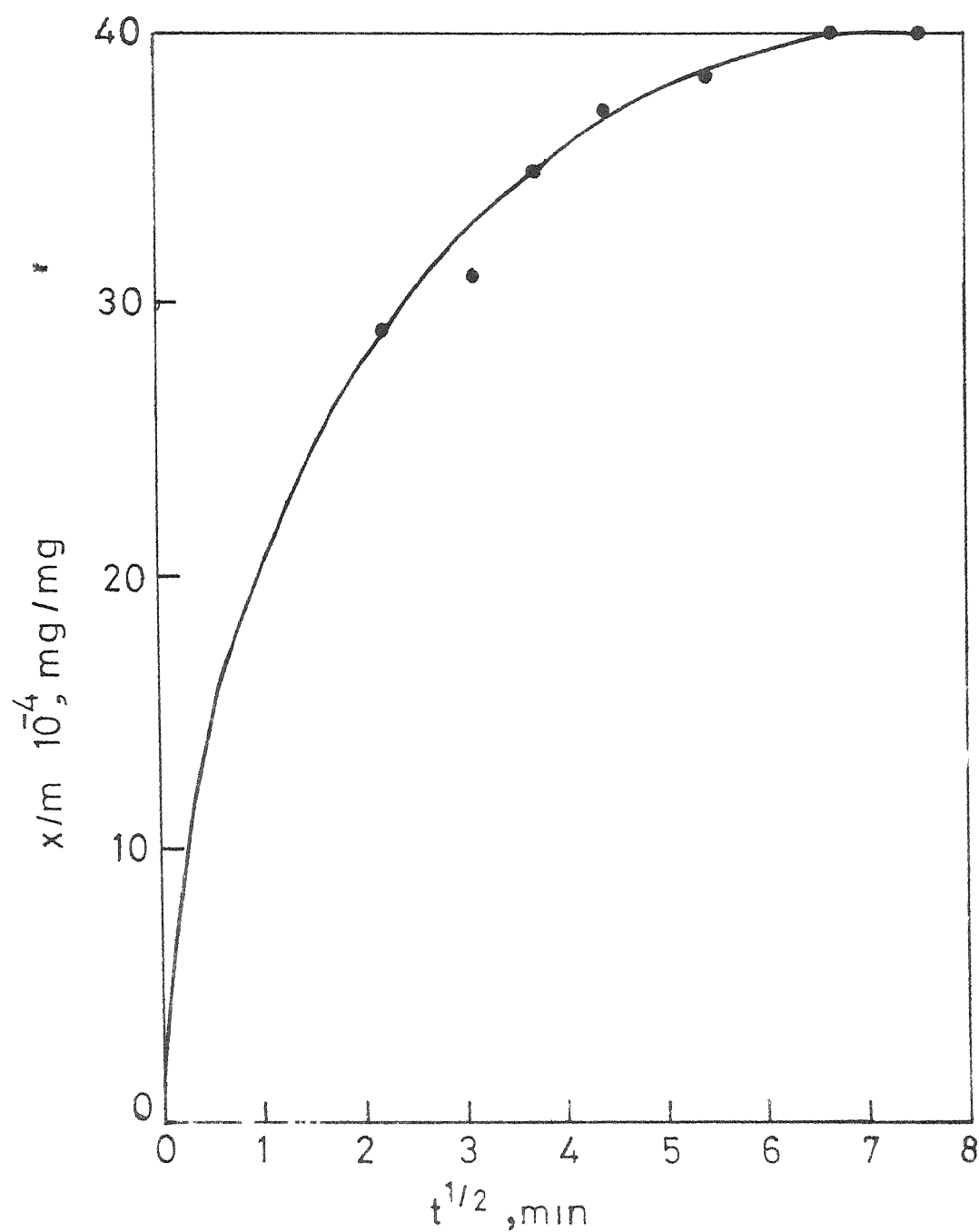
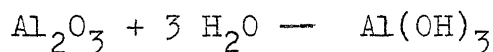


FIG 5.4 PLOT OF HALF POWER OF TIME Vs.  
FLUORIDE ADSORBED ON ACTIVATED  
ALUMINA

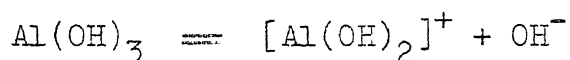
### 5.2.2 Effect of Various Parameters:

(a) pH. The pH of the water has a marked effect on the fluoride removal capacity of activated alumina. Removal capacity is found to be higher at pH values lower than 6 and decrease at pH higher than 8. Capacities are reasonably constant in pH range 6-8 (Fig. 5.5).

This effect can be explained on the basis of  $\text{OH}^-$  group activity. A small amount of moisture present in atmosphere, get adsorbed onto activated alumina and gets ionised.  $\text{OH}^-$  ion adsorbed at the cationic sites ( $\text{Al}^{3+}$ ) and proton to anionic sites ( $\text{O}^-$ ) producing surface hydroxyl groups (Hofmann, 1975).



At lower pH, these  $\text{OH}^-$  may come out to neutralise the acidity present, leaving the cationic sites for fluoride adsorption



This is supported by finding that alumina causes an increase in pH when added to a low pH water.

At higher pH, when  $\text{OH}^-$  are present in higher concentrations, there is a competition between  $\text{OH}^-$  and fluoride for the active sites on the surface of alumina. Activated alumina has more affinity for  $\text{OH}^-$  as compared to fluoride ion (Kubli, 1947).  $\text{OH}^-$  group from the solution gets adsorbed on the cationic sites thus blocking the active sites for fluoride adsorption.

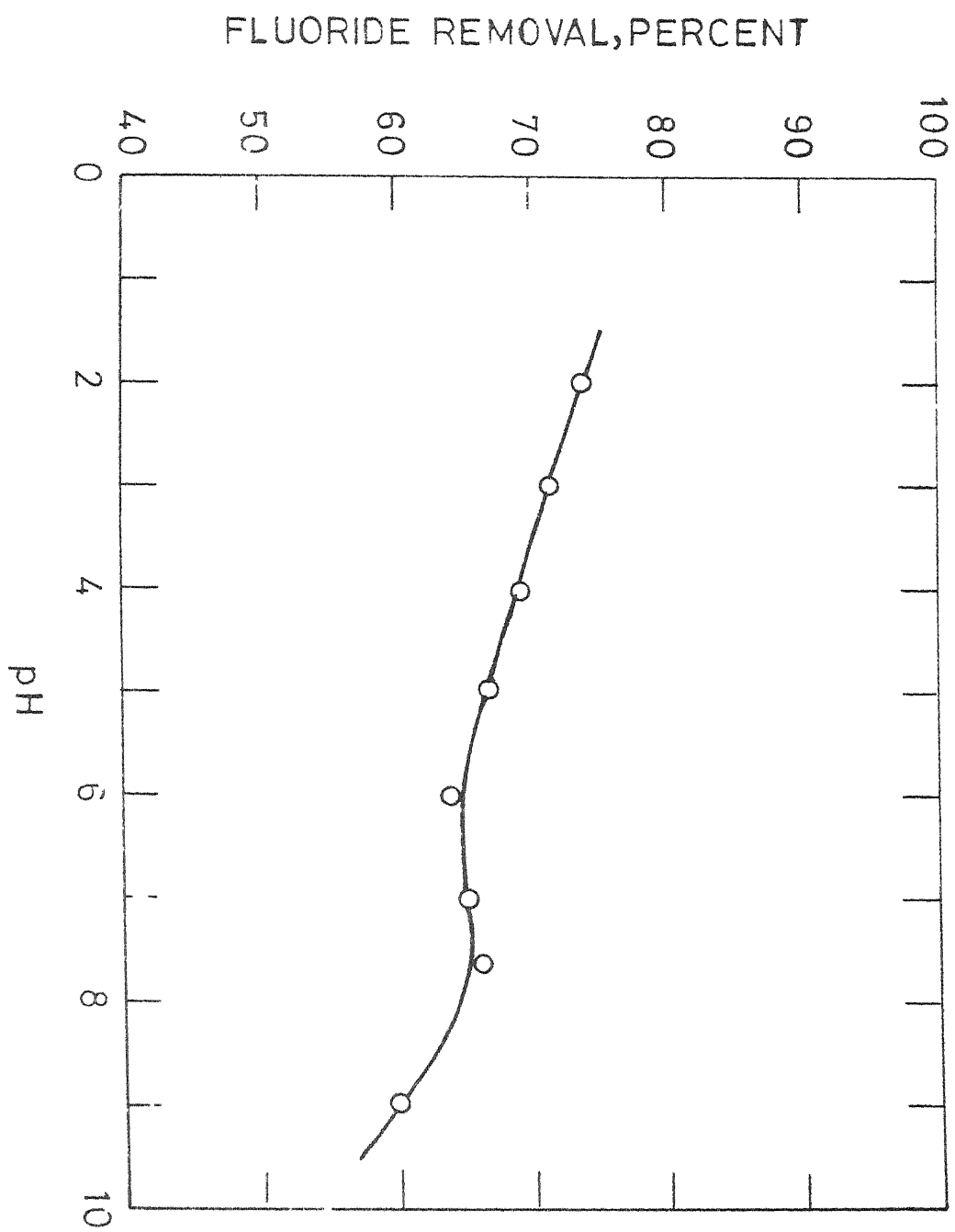


FIG.5.5 EFFECT OF pH ON FLUORIDE REMOVAL

Similar are the findings of Bishop et al. (1975) who observed higher removal at pH value lower than 6 and reasonably good removal from pH 6-8.

(b) Alkalinity. Alkalinity of the raw water plays a very significant role in the fluoride removal. Results presented in Fig. 5.6 show that there is an inverse relationship between the fluoride removal efficiency and alkalinity. Higher removal efficiencies are found from waters having low alkalinity. Around 55 per cent reduction in efficiency was observed at 500 mg/l (as  $\text{CaCO}_3$ ) alkalinity. Adverse effect of alkalinity was also observed by Theragaonkar et al. (1969) and Bishop et al. (1975). Up to 75 per cent reduction in fluoride removal was found at alkalinity values 500 mg/l (as  $\text{CaCO}_3$ ).

Alkalinity of the raw water decreases when water was kept in contact with activated alumina, suggesting that  $\text{HCO}_3^-$  competes with fluoride ion for the active sites on the media reducing the fluoride removal efficiency.

(c) Particle size: The effect of particle size on the removal of fluoride was studied in order to determine the most efficient particle size (Fig. 5.7).

Results show that removal capacity increases with decrease in particle size. The greater removal efficiency of small size media is naturally due to greater surface area per unit volume

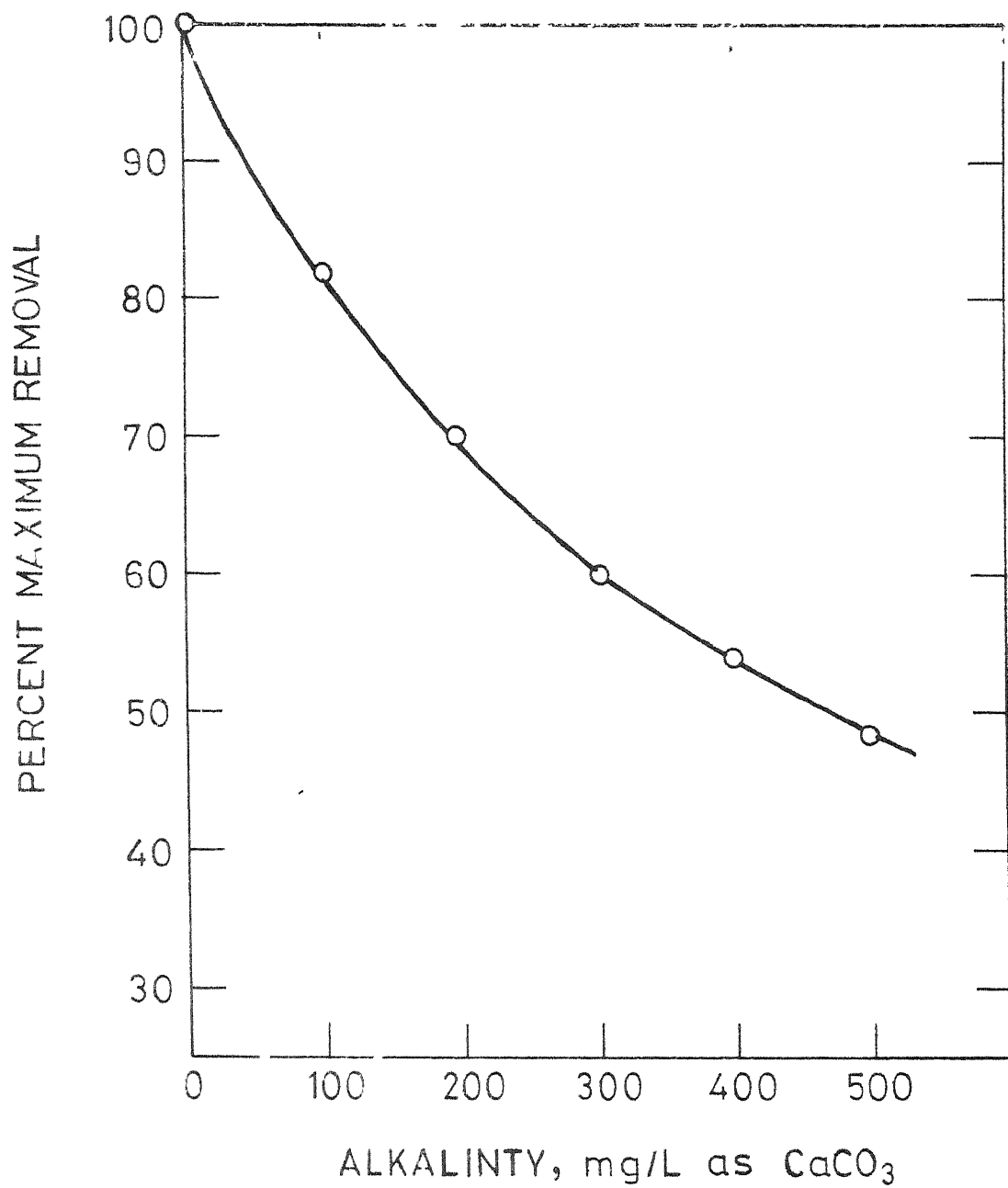


FIG.5.6 EFFECT OF ALKALINITY ON FLUORIDE REMOVAL

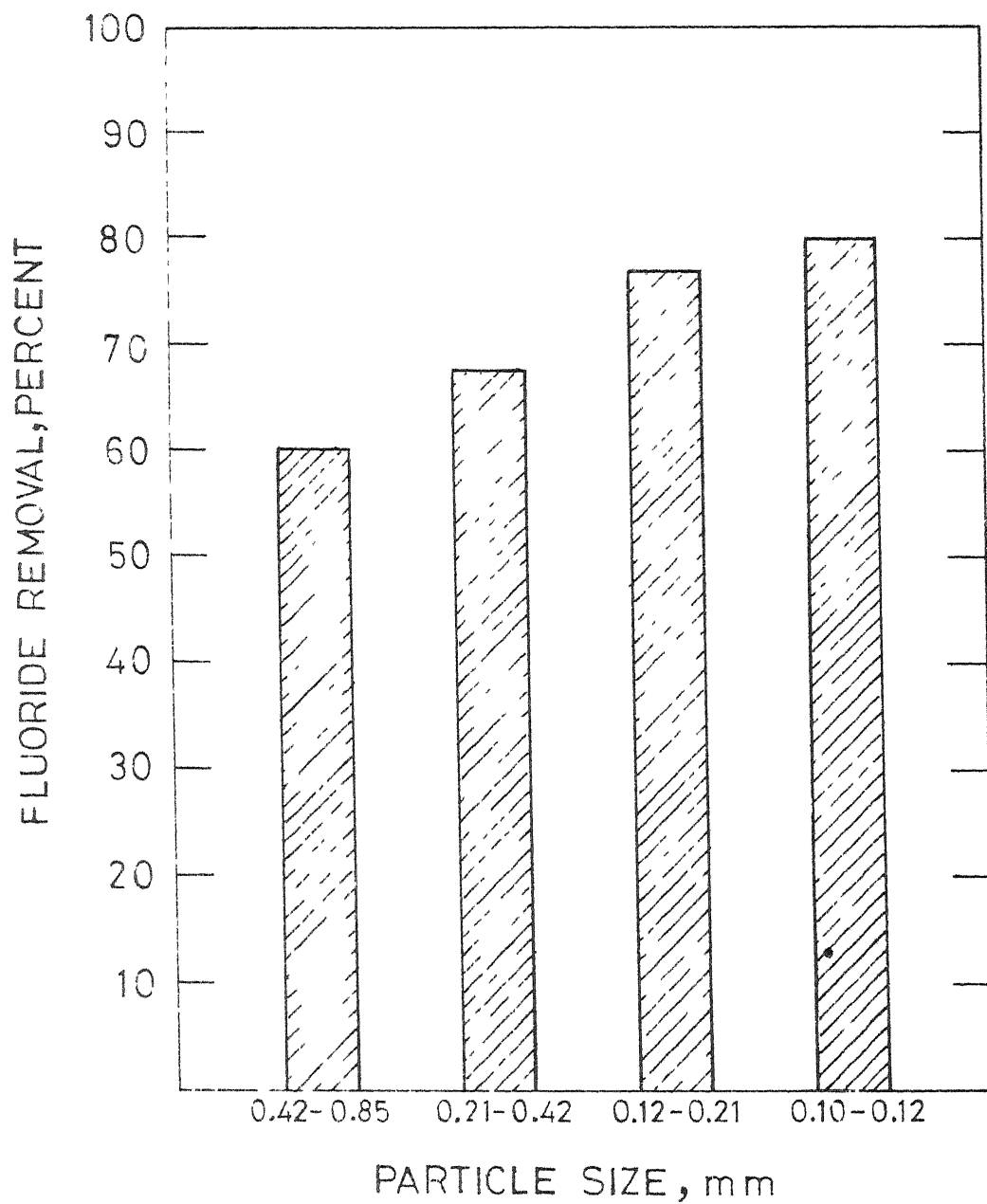


FIG.5.7 EFFECT OF PARTICLE SIZE ON FLUORIDE REMOVAL

This indicates that fluoride removal by activated alumina is a surface phenomenon. A smaller size would be more efficient for fluoride removal but will be less useful for continuous flow studies. The maximum removal with the finest particle that could be obtained in the laboratory was 80 per cent. In view of the continuous flow studies the materials were taken in columns to study only the flow rates of water. It was observed that with the finest particle size the flow was less than 30 lpm/sq.m., while with 0.12-0.21 particle size gave a flow rate of approximately 70 lpm/sq.m. With 0.21-0.42 particle size the flow was found to be more than 140 lpm/sq.m. Hence this particle size was chosen for batch as well as continuous flow experiments.

(d) Initial fluoride concentration: Results indicate that removal capacity is a function of initial fluoride concentration and increase with the increase in fluoride concentration (Fig. 5.8). Similar results were observed by Bishop et al. (1975). They got a linear relationship between fluoride concentration and removal.

After an initial concentration of 10 mg/l, per cent removal is found to be constant.

### 5.3 Continuous Flow Studies:

After studying various factors affecting the fluoride removal, continuous flow for the removal of fluoride. Fluoride



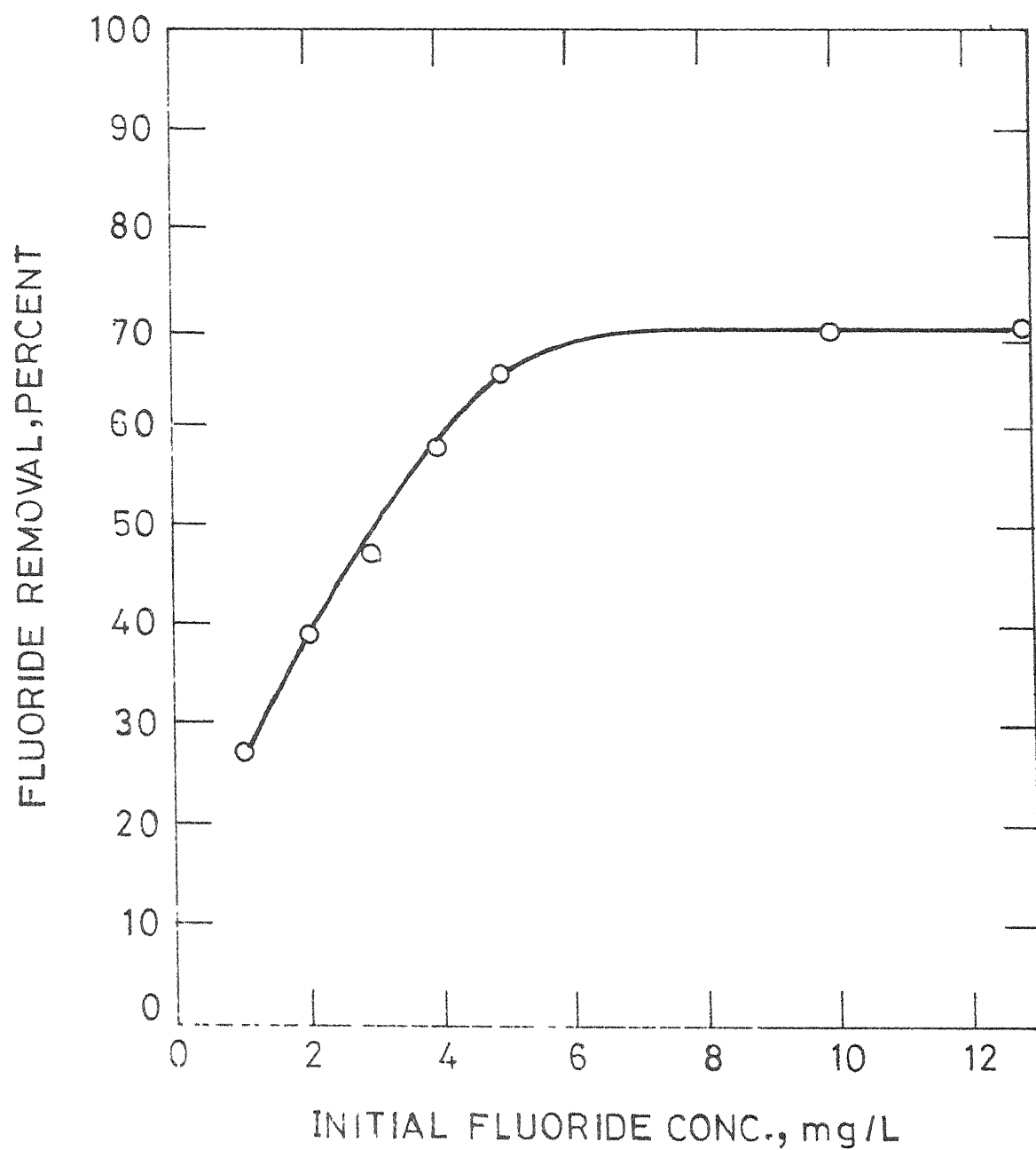


FIG.5.8 EFFECT OF INITIAL FLUORIDE CONC.  
ON FLUORIDE REMOVAL

solution was passed at a flow rate of 37 lpm/sq.m. through a bed of activated alumina and fluoride concentration was measured in the effluent.

### 5.3.1 Effect of Loading Rate:

Fluoride removal efficiency of alumina was studied at loading rates of 37 lpm/sq.m , 70 lpm/sq.m . and 140 lpm/sq.m. Results indicate that at higher flow rates, column can be operated for less duration. However, break through capacities were found to be constant (around 50 mg /10 gm of alumina) for all flow rates, suggesting that removal of fluoride by activated alumina is a surface phenomenon.

### 5.3.2 Regeneration:

Regeneration was carried out with 0.1N HCl, 0.1N  $H_2SO_4$  and 1 per cent alum solution when a leakage of 1.5 mg/l. fluoride was observed in the effluent during the course of column run. 500 ml of HCl,  $H_2SO_4$  and alum, which was found to be optimum was passed through the column at a rate of 100 ml/hr.

The effect of regeneration with these materials on the fluoride removal efficiency of activated alumina is shown in Fig. 5.9. After a series of preliminary studies conducted with distilled water, experiments were conducted to study the removal efficiency in natural water. Fluoride solution (6.5 mg/l) prepared in tap water was employed for these purposes.

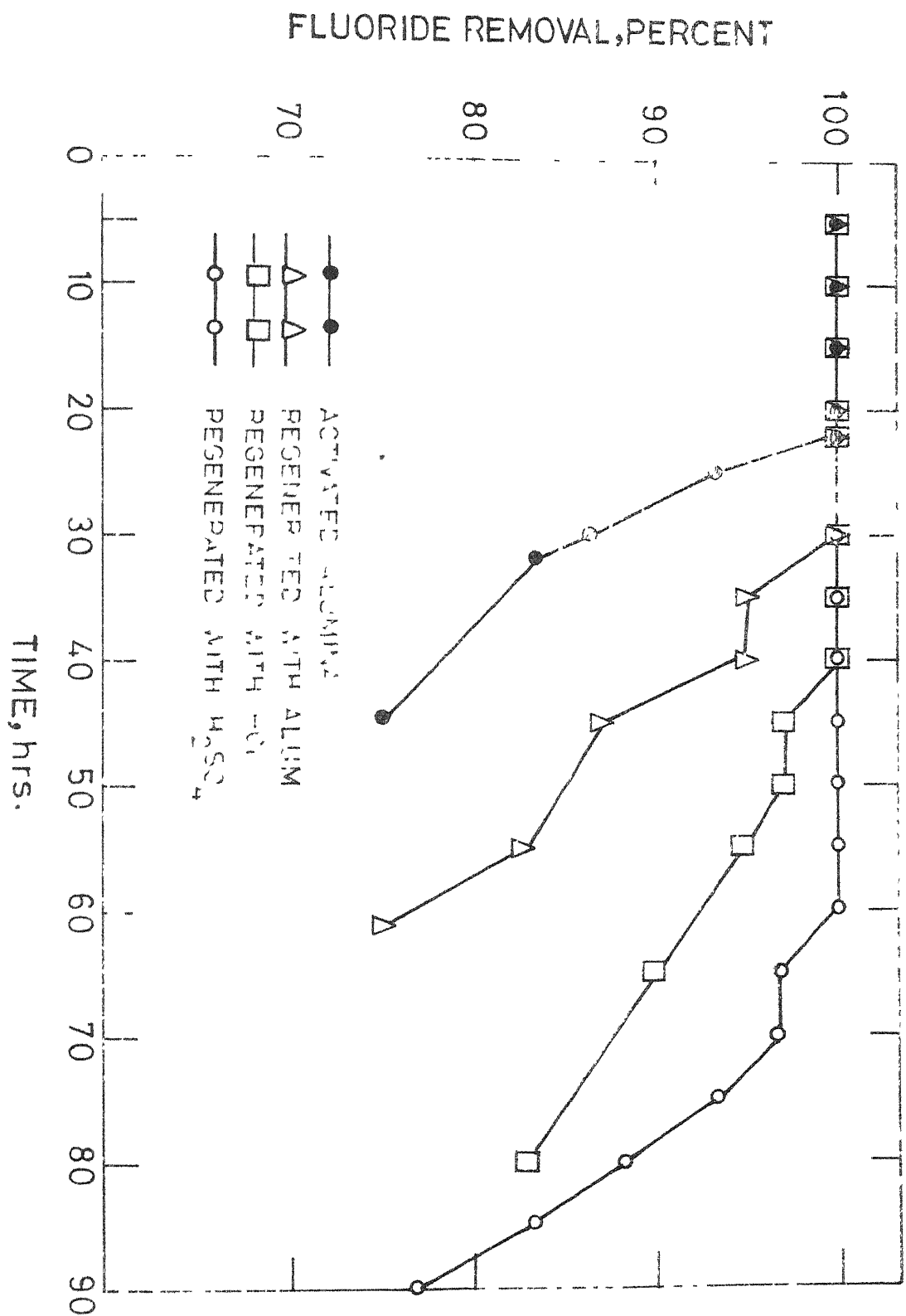


FIG. 5.9 EFFECT OF DIFFERENT REGENERANTS USED ON FLUORIDE REMOVAL CAPACITY

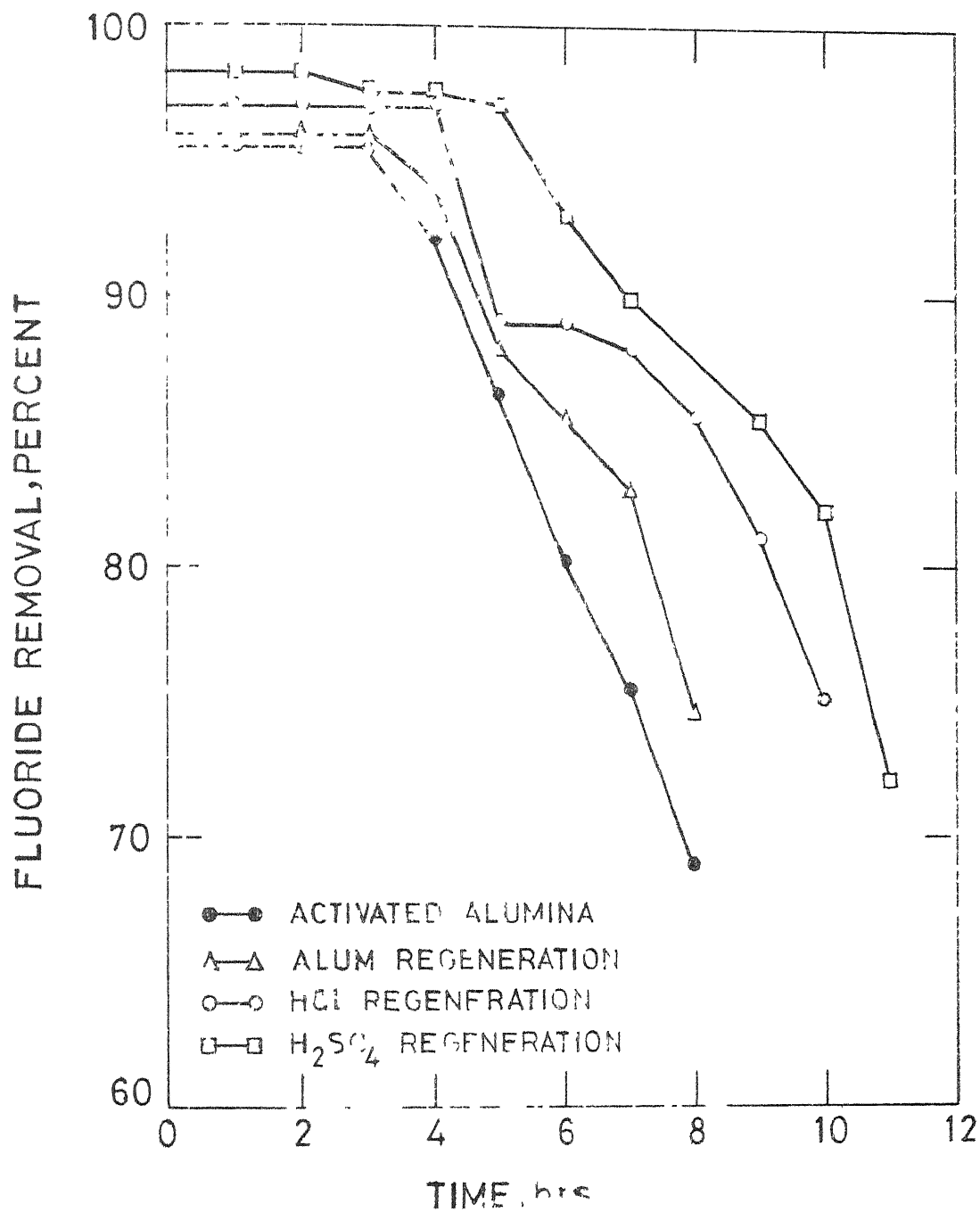


FIG. 5 10 EFFECTS OF DIFFERENT REGENERANTS ON FLUORIDE REMOVAL EFFICIENCY

Columns were operated at a flow rate of 140 lpm/sq.m. Removal efficiency of activated alumina, before and after regeneration, are shown in Fig. 5.10.

Break through capacities were calculated for both types of test water and are shown in Table 3. Results clearly indicate a reduction in fluoride removal efficiency when tap water was used for preparation of sample. This reduction is due to alkalinity in raw water which interfered with removal of fluoride by activated alumina.

An interesting fact noted during the experiment was the increase of fluoride removal capacity after first cycle of regeneration. The actual mechanism is not known. It may be due to the activation of alumina after fluoride adsorption which results in an increase in active sites on alumina surface or may be due to adsorption of excessive  $H^+$  from regenerant solution, resulting in an increase in number of cationic sites for adsorption of fluoride.

15 cycles of regeneration were carried out using 0.1N HCl and 0.1N  $H_2SO_4$ . Results shown in Fig. 5.11 indicate that  $H_2SO_4$  is the most effective regenerant. It has been reported that treatment of alumina with acid ( $HCl$ ,  $H_2SO_4$ ) apparently produces a surface consisting of both co-valently bound and ionized ion. Formation of ionized form is favored by an increase in acid concentration. The substrate in this condition will be able to behave as an ion-exchanger,  $Cl^-$  and

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Table 3: Effect of Regeneration on fluoride removal efficiency.

Regeneration	Break through capacity mg/10 gm of alumina	
	Fluoride in distilled water	Fluoride in Tap water
Activated alumina	45	20
After HCl regeneration	60	25
After $H_2SO_4$ regeneration	70	28
After alum regeneration	50	22

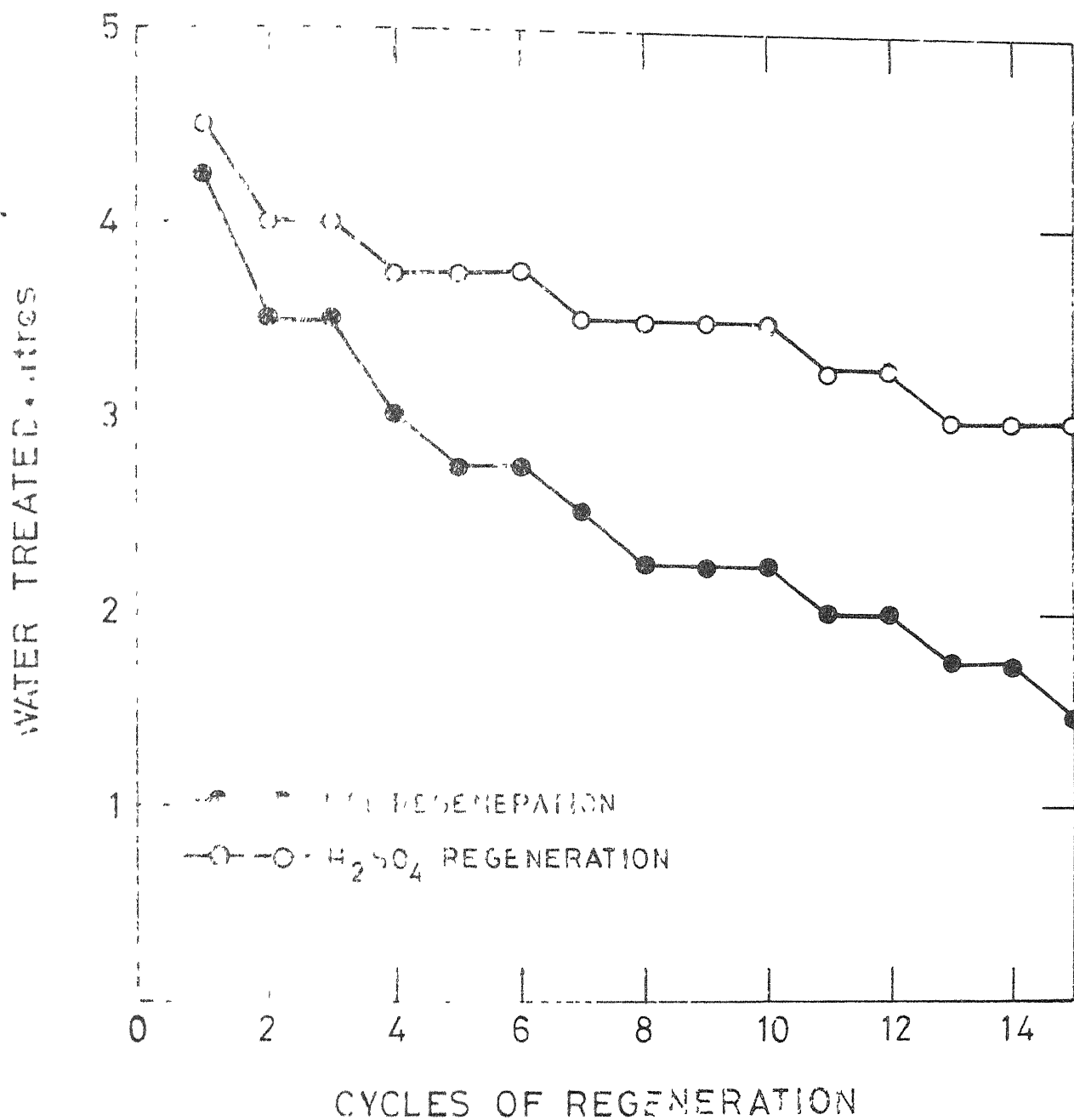


FIG 5.11 EFFECTS OF REGENERATION CYCLES ON FLUORIDE REMOVAL CAPACITY OF ALUMINA

and  $\text{SO}_4^{=}$  exchanging with fluoride ion in the applied solution (Heftmann 1963). The high removal efficiency of  $\text{H}_2\text{SO}_4$  regenerated columns can be explained on the basis that entering fluoride ion displaces both covalently bound and ionized  $\text{SO}_4^{=}$  while in the case of HCl regeneration it will replace mainly ionized  $\text{Cl}^-$ , therefore after each cycle of regeneration covalently bound chloride will increase on the surface of the activated alumina, resulting in a decrease in the removable  $\text{Cl}^-$ . As a result of it efficiency goes down very fast after each regeneration (Giles et al. 1954, 1959).

Clogging problem was observed when alum was used for regeneration which may be due to its precipitation in the bed (Bishop et al. 1975).

### 5.3.2 Optimum Concentration of Sulphuric Acid.

Figure 5.12 presents the experimental results of column regeneration by different concentration of sulphuric acid. It appears that concentration beyond 0.1N does not result in any significant increase in the removal of fluoride. Therefore, 0.1N  $\text{H}_2\text{SO}_4$  was selected as the optimum concentration. However, at 0.5N  $\text{H}_2\text{SO}_4$  concentration, removal efficiency of the column was found to decrease which may be due to change in surface groups of alumina at such high concentration of acid, since some dissolution of alumina was observed.



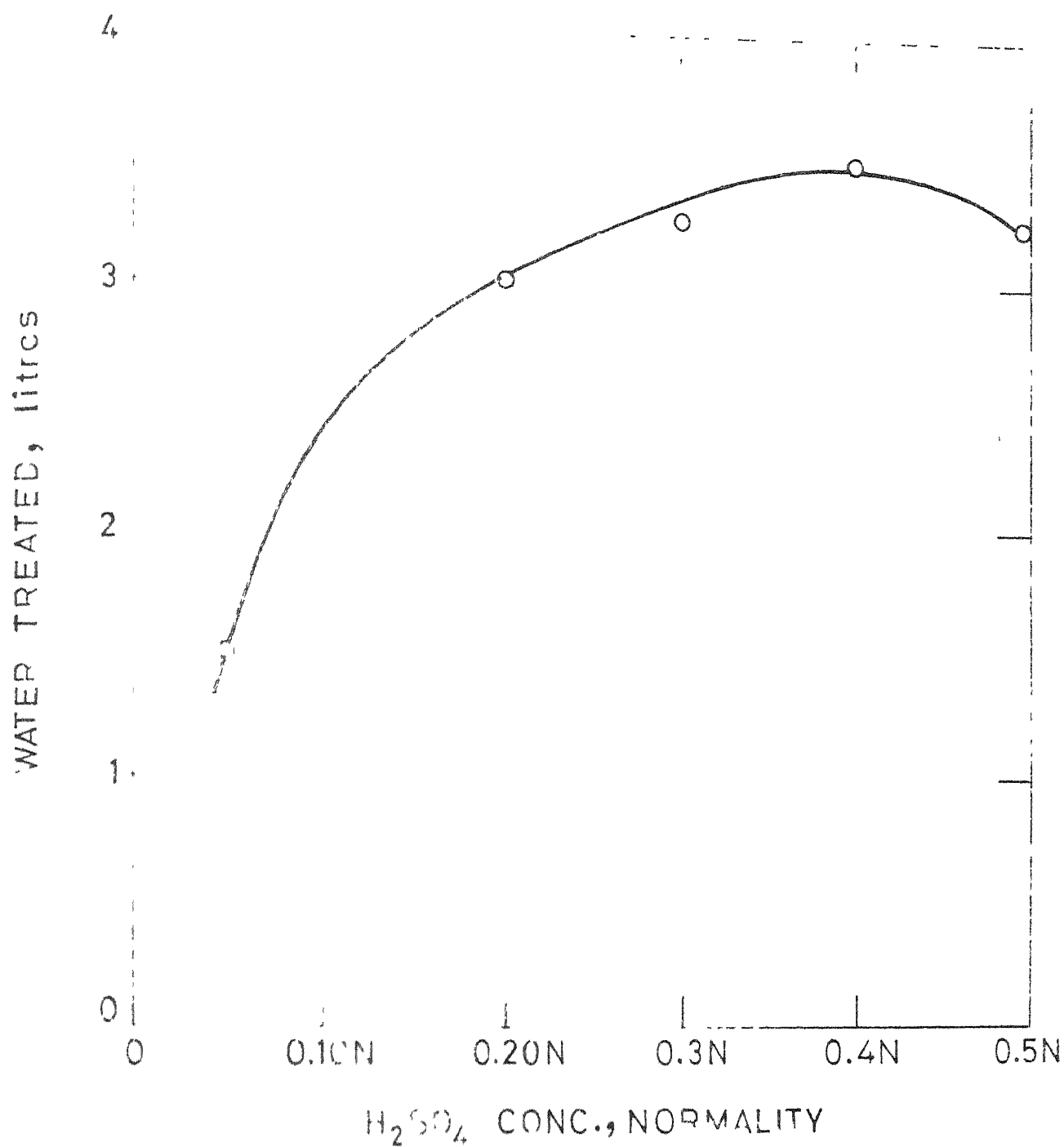


FIG 512. EFFECT OF REGENERANT CONC. ON  
FLUORIDE REMOVAL CAPACITY

Observations on regeneration with different bed volumes of sulphuric acid for different contact times are reported in Table 4. Results show a lesser efficiency of column for fluoride removal but this method of regeneration is found to be very convenient, practicable as the time required is relatively small. Also, a comparatively smaller amount of acid is required for regeneration. One bed volume for one hour of contact time was selected for regeneration as no significant increase in fluoride removal was found when more bed volumes of the acid was used.

Five cycles of regeneration with one bed volume of acid were tried and 40 per cent reduction in the fluoride removal efficiency was observed. The rapid decrease in the efficiency is due to incomplete regeneration of bed by one bed volume of acid. Further, it was found exhausted bed can be regenerated completely by placing the alumina in 0.1N  $\text{H}_2\text{SO}_4$  solution overnight. Experiments were carried out and alumina was found to restore the efficiency approximately equal to original. The completely regenerated alumina could be again used for fluoride removal.

After a preliminary experiments with small columns, to provide information for the design of small house-hold defluoridating unit, experiments were carried out with large size column. Fluoride removal efficiency was found to be better

Table 4. Regeneration of column by different  
bed volumes of acid

Bed volumes of $\text{H}_2\text{SO}_4$ used	Contact time hr.	Total water treated litres
1	0.5	2.5
1	1.0	3.0
2	1.0	3.25
2	2.0	3.5
3	1.5	3.75
3	3.0	3.75
After complete regeneration		4.5

When 500 ml of 0.1N  $\text{H}_2\text{SO}_4$  is passed at a flow rate rate  
of 150 ml/hr.

with large column as 65 litres of water could be treated per 100 gm of alumina (5.25 gm/kg, 83 gr/cu.ft, 1408 grains/cu.ft). The fluoride removal efficiencies, earlier reported, are 295 grain/cu.ft (Boruff, 1934), 505 grain/cu.ft (Swope and Hess, 1937), 416 grains/cu.ft (Tink and Lindsay, 1938), 380 mg/kg (Thergaonkar, 1969) and 1000 grain/cu.ft (Bishop et al., 1975). Reduction of 70-80 per cent was reported by these authors at 500 mg/l alkalinity. It reveals that the present method is very efficient for the defluoridation of water as comparative to existing methods and can be successfully used in the field.

The cost of the alumina used in the unit was Rs 1.5 (15 rupees/kg of alumina) and regeneration cost worked out to be one paise per cycle (considering the cost of acid only).

## 6. SUMMARY AND CONCLUSIONS

On the basis of the present study, following conclusions have been drawn.

1. Among the various adsorbents screened for the removal of fluoride from drinking water, activated alumina is found to be best.

2. Although higher removal efficiencies were achieved at pH value lower than 6, efficiencies were reasonably good in the pH range 6-8.

3. Alkalinity of the raw water adversely affects the fluoride removal capacity. At alkalinity 500 mg/l (as  $\text{CaCO}_3$ ), fluoride removal capacity was reduced by 55 per cent as compared to distilled water.

4. Efficiency of fluoride removal is a function of initial fluoride concentration upto 10 mg/l. Above this per cent removal remained constant.

5. Total capacity of alumina for fluoride removal remained unchanged for different loading rate (37 lpm/cu.ft., 70 lpm/cu.ft. and 140 lpm/cu.ft). However, duration of column run decreased linearly with the flow indicating that adsorption of fluoride on the activated alumina is mainly a surface phenomenon. The similar conclusions were also drawn from adsorption studies.

6. Exhausted columns were regenerated using HCl,  $H_2SO_4$  and alum and 0.1 N  $H_2SO_4$  was the most efficient.

7. Column regenerated with one bed volume of acid show a lower removal efficiency but is very convenient and practicable. Further it is found that original efficiency can be restored by keeping exhausted alumina in 0.1N  $H_2SO_4$  overnight.

Based on the results of this study, it is felt that further work should be carried out on these lines:

1. Alkalinity removal greatly enhances the efficiency of defluoridating material, thus bringing down the cost of system. Hence methods can be tried for the removal of alkalinity as preliminary to fluoride removal.

2. For each regeneration cycle, fresh sulphuric acid was used in the present study. Attempts should be made for the use of acid for successive regeneration cycles.

3. At initial stages of column run, there will be a complete removal of fluoride from water which will require the mixing of raw water to bring the optimum fluoride concentrations. A unit should be designed in a manner so that raw water will be mixed to the effluent to get desired fluoride concentration.

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